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Halogen–Metal Secondary Bonding. 2.[1] A Variable-Temperature and -Pressure Nuclear Quadrupole Resonance Study of Inter- vs. Intramolecular Secondary Bonding in Mercury Derivatives of Chlorocarbons

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The temperature and pressure dependence of the ^{35}Cl NQR spectra of a number of mercury derivatives of chlorocarbons are used to study secondary bonding of the chlorine and mercury atoms. It is proposed that the NQR splitting caused by intramolecular secondary bonding should be independent of T and P; splitting due to intermolecular secondary bonding should increase at lower temperatures and higher pressures. These criteria suggest that secondary bonding, when present, is intermolecular in (*trans*-2-chlorovinyl)-, (trichloromethyl)-, and (pentachlorocyclopentadienyl)mercurials, while it is usually intramolecular in (pentachlorophenyl)- and (2,6-dichlorophenoxy)mercurials.

Introduction

A variety of evidence[5-12] suggests that halogen atoms bonded to carbon may show a weak additional interaction with metal atoms in the same or in other molecules. Alcock has suggested the term "secondary bonding" to describe this effect.[13] Little is known as to the detailed nature of this interaction, even though such interactions might be important in such reactions as heavy metal ion catalyzed displacement reactions of alkyl halides,[6b] the generation of carbenes,[14] or the decomposition of metal chlorophenoxides to yield chlorodioxins or chloropolyphenylene oxides.[15]

In the solid state, this secondary interaction may be either intermolecular or intramolecular. Although X-ray crystallography can distinguish these, few crystal studies are available for metal derivatives of chlorocarbons. Halogen NQR is a very sensitive and relatively fast method of probing the electronic environments of halogen atoms, and it has been used to investigate the nature of secondary bonding in group 5 metal trihalides.[16-22] Theory leads us to suspect that the variable-temperature and -pressure NQR methods used in that study could distinguish inter- from intramolecular secondary bonding. In this paper we investigate, by variable-temperature and -pressure NQR, mercury derivatives of chlorocarbons having different numbers of atoms between the mercury and chlorine atoms. These atoms will create geometries either favorable or unfavorable to intramolecular ring formation, so that the NQR results should then be a function of the ring size. In some cases X-ray studies are available to clarify the interpretation. The classes of compounds being studied are shown in Table I. The compounds have been classified according to the size of the ring formed if intramolecular secondary bonding occurs: three-membered rings in classes **2** and **3**, four-membered rings in classes **3** and **4**, and five-membered rings in classes **5**, **6**, and **7**. If the secondary bonding is a type of coordinate covalent bonding, chemical experience would lead us to expect the strongest intramolecular bonding in five-membered rings; intermolecular interactions could occur in any of these classes.

Theory

Several works cover the theory of nuclear quadrupole resonance (NQR) and the trends of NQR frequencies of organohalogen compounds.[23-27a] From the Townes–Dailey theory it may be predicted, and it is observed, that the NQR frequency of an organochlorine atom which engages in intermolecular or intramolecular secondary bonding shows a lowered NQR frequency as a result.[5,18,27b] One would also expect that any process which increases the average metal–chlorine distance would reduce this interaction and thereby restore the chlorine NQR frequency (ultimately) to the frequency of a noninteracting chlorine.

If a solid possesses intermolecular metal–chlorine interactions which extend in one or more dimensions throughout a crystal, compression of the crystal along that direction would increase metal–chlorine interactions. Such compression can usually be expected upon (1) lowering the temperature or (2) raising the pressure on the crystal. Hence we would normally expect the frequency lowering which results from intermolecular secondary metal–chlorine bonding of an extended type to be reduced at higher temperatures but increased at higher pressures.

An NQR shift due to intramolecular metal–chlorine secondary bonding is not affected systematically by changes in temperature or pressure, unless the average metal–chlorine distance is changed. This postulate is the basis for distinguishing inter- and intramolecular effects using NQR.

Where feasible we have studied compounds which have several chlorine atoms in positions which are chemically equivalent but which can be rendered nonequivalent by secondary bonding. In such cases we expect to see a substantial splitting (>1–2%)[25,28] of the NQR frequencies of these otherwise equivalent chlorines. This splitting is expected to be reduced at higher temperatures in the case of intermolecular secondary bonding but not in the case of intramolecular secondary bonding

A caveat needs to be observed here, however: the temperature dependence of NQR frequencies in molecular crystals is usually determined by the mean-square amplitude of thermal oscillations of the chlorine-containing group in the molecule.[24] Chemically equivalent chlorines sitting in crystallographically distinct positions need not have the same amplitude of oscillation, regardless of any question of lattice expansion or secondary interactions. It will be assumed that the amplitudes of these oscillations, and therefore the magnitudes of the temperature dependence, vary independently of the 77 K NQR frequency for chemically equivalent chlorine atoms in molecules with no secondary bonding. In order to see whether this assumption is true, we have measured or taken from the literature[5,29-41] the results of variable-temperature NQR measurements on organic derivatives in classes **2**–**7** (Table II), which do not have metal atoms or the possibility of hydrogen bonding.

Experimental Section

^{35}Cl NQR spectra were measured on a Decca Radar NQR spectrometer using Zeeman modulation, at different temperatures which were achieved using standard slush baths. Spectra were normally recorded at three or four temperatures, which is not enough to be absolutely certain that phase transitions, which would give anomalous temperature dependences, were absent. However, it would be quite surprising if all or most of the compounds in a given class showed undetected transitions, each having a similar effect on the temperature dependence, so that a false trend would be observed.

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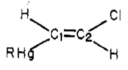
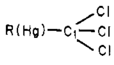
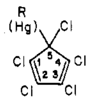
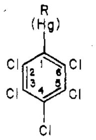
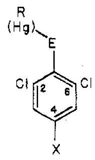
Table I. Classes of Compounds Studied and NQR Expectations[a]

						
			3			**5**, E = O, X = H 6, E = S, X = H 7, E = O, X ≠ H
	1	**2**	allylic	vinylic	**4**	
intramolecular secondary bonding may involve Cl no.		1	5	1 and 4	2 and 6	2
intermolecular secondary bonding may involve Cl no.	2	1	5	any Cl	any Cl	2 and/or 6
NQR pattern[a] resulting from						
(a) no secondary bonding	1 line	1 line	1 line[b]	2 close lines[b]	1 line[b]	1 line or 2 very close lines
(b) intramolecular secondary bonding		1 line	1 line[b]	2 close lines[b]	1 line[b]	2 lines
(c) intermolecular secondary bonding[c]	1 or 2 lines	1 or 2 lines	1 or 2 lines[b]	additional splitting[b]	additional splitting[b]	1 or 2 lines

[a] Ignoring additional small (<0.8 MHz[25,28]) splittings due to lowered symmetry in the lattice or to the presence of more than one type of molecule in the unit cell. [b] Plus lines due to other types of chlorine in the molecule. [c] Including the possibility that only some of the molecules in the unit cell engage in intermolecular secondary bonding.

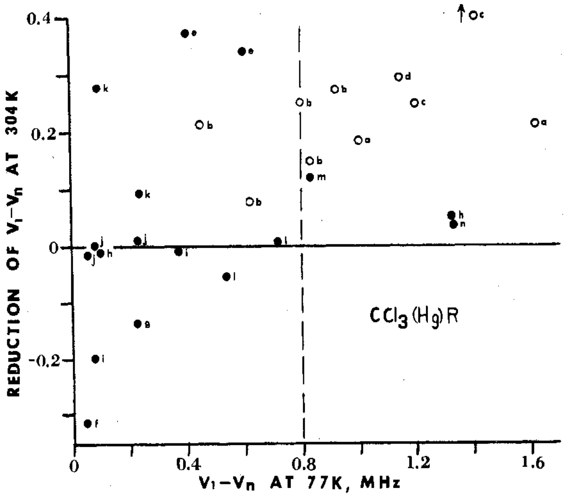


Figure 1. NQR frequency splittings at 77 K ($\nu_1 - \nu_n$, see eq 1) for trichloromethyl compounds (**2**) compared with the reduction of those splittings (see eq 2) at 304 K. Data for mercurials are shown with open circles, and data for nonmercurials are shown with closed circles. Letters refer to individual compounds listed in Table II, which includes literature references. (The reductions of splitting are often extrapolated from lower temperature data, since many of these compounds melt or show rapid hindered reorientation of the CCl_3 group below 304 K.)

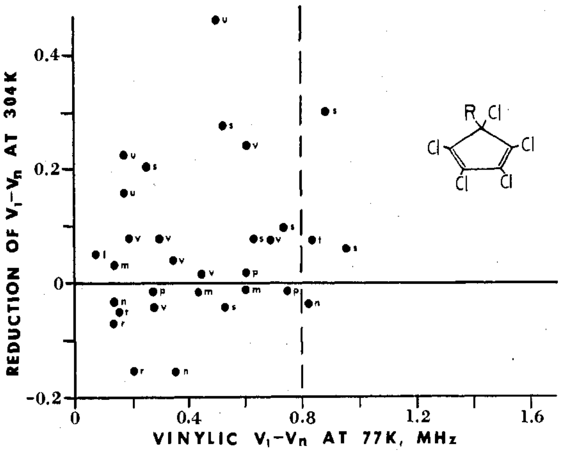


Figure 2. NQR frequency splittings at 77 K of vinylic chlorines (chlorine number 1–4) of nonmercurial pentachlorocyclopentadienyls (**3**) compared with the reduction of those splittings at ambient temperature (about 304 K). (The reductions of splitting are often extrapolated from lower temperature data, since many of these compounds melt below 304 K.)

Frequencies are accurate to ±0.007 MHz. In cases of weak signals, room-temperature spectra were also observed (±0.06 MHz) on the more sensitive Wilks NQR-1A spectrometer. Pressure dependences were obtained using a conventional superregenerative oscillator and an oil-filled pressure system.[18]

The compounds included in this study are listed in Table II. The preparations and NQR spectra of compounds of classes **1**, **2**, and **3** were reported previously. We attempted to prepare the compounds CCl_3HgI, $CCl_3HgCH_2C_6H_5$, and $CCl_3HgC_6H_2(CH_3)_3$-2,4,6, but our products failed to give NQR spectra and were not investigated further.

Bis(pentachlorophenyl)mercury (**4a**) was purchased from Orgmet; another sample was obtained from Dietmar Seyferth. Compounds **4b** and **4e** were prepared from the commerical **4a** by literature methods,[42] but the latter failed to give an NQR spectrum. Compound **4c** was prepared analogously to the chloride and had a melting point of ca. 260 °C and an IR spectrum similar to that of other members of class **4**. Anal. Calcd: C, 13.60; Hg, 37.86. Found: C, 13.71; Hg, 37.67 (Galbraith Labs). Compound **4d** was obtained by recrystallizing **4b** from dioxane; it was analyzed by pumping on a weighed sample to constant weight; dioxane was lost very readily. Calculated loss of dioxane for $C_6Cl_5HgCl{\cdot}C_4H_8O_2$: 15.4%. Found: 11.6, 10.4, 9.8%. The percent dioxane found decreased with age of the sample, suggesting rapid loss from the fresh product. DTA was not available to investigate the composition of freshly prepared, moist samples. No adduct could be prepared by recrystallizing **4b** from 1,2-dimethoxyethane.

Mesitylmercury acetate was prepared by literature methods[43] from Aldrich Gold Label mesitylene, but products prepared from it failed to give NQR spectra; (2,4,6-triisopropylphenyl)mercury acetate was prepared analogously. (4-(Dimethylamino)phenyl)mercury acetate and benzylmercury hydroxide were prepared by literature methods; phenylmercury hydroxide was purchased from Aldrich. The corresponding 2,6-dichlorophenoxides were prepared by reaction of the acetates with sodium 2,6-dichlorophenoxide in alcohol or water, or by reaction of the hydroxide with 2,6-dichlorophenol in alcohol, and were recrystallized by literature methods.[36]

Results and Discussion

Variable-Temperature Experiments. The new ^{35}Cl NQR spectral results are reported in Table III. Literature sources of other variable-temperature data are reported in Table II.

Table II. Compounds Included in the Study

	mercurials studied			nonmercurials studied			
class	no.	R	ref[a]	no.	X	R (omit Hg)	ref[a]
1		Cl	5				
2	a	CCl_3	5	e		$CH(OH)(OC_2H_5)$	29, 35
	b	C_6H_5	5	f		H	29, 30
	c	Cl	5	g		CH_3	29, 30
	d	Br	5	h		$CH(OH)_2$	29, 31
				i		$CH(OH)(NH_2)$	29
				j		CCl_3	29
				k		$CH(OH)(OCH_3)$	29, 35
				l		c-$C_8Cl_4(CCl_2)_2(CCl_3)$	32
				m		C_6H_4Cl-4	33
				n		C_5Cl_5	5, 34
3	a	C_5Cl_5-γ	5	l		$C(CH_3)_3$	5
	b	Cl-γ	5	m		C_2H_5-α	5
	c	Cl + glyme[b]	5	n		C_2H_5-β	5
	d	Br + glyme[b]	5	p		$CH_2C_6H_5$	5
	e	Cl + diglyme[b]	5	r		H	5
	f	C_6H_5	5	s		C_5Cl_5	5
	g	$CH_2C_6H_5$	c	t		CCl_3	5
	h	C_5Cl_5-α	5	u		Cl-α	5
	i	$Cl{\cdot}HgCl_2$	5	v		Cl-β	5
	j	$Br{\cdot}HgBr_2$	5				
	k	Br	5				
4	a	C_6Cl_5	c, d	g		$N(CH_3)_2$	29
	b	Cl	c, d	h		COCl	29
	c	Br	c, d	i		SCH_3	29
	d	Cl + dioxane[b]	c, d	j		COOH	29
	e	C_6H_5	d	k		C_6Cl_5	e
	f	CH_3	d	l		C_2H_5	e
				m		OCH_3	e
				n		Cl	e
				p		F	e
				r		SO_2Cl	e
				s		$NHCH_3$	e
				t		NH_2	e
				u		OH	e
				v		SH	e
				w		H	e
5	a	C_6H_5	c, 36	e		CH_3	37
	b	$CH_2C_6H_5$	c, f	f		H	38
	c	$C_6H_2[CH(CH_3)_2]_3$-2,4,6	c, f				
	d	$C_6H_4N(CH_3)_2$-4	c, f				
6	a	C_6H_5	39	b		CH_3	39
7				a	F	H	37
				b	CN	H	37
				c	NH_2	H	37
				d	Cl	H	38
				e	I	H	37
				f	CHO	H	37
				g	CH_3	H	37
				h	F	CH_3	37
				i	NO_2	CH_3	37

[a] Footnote, or literature reference number for temperature-dependent NQR work. [b] Coordinated to Hg (glyme = $CH_3OCH_2CH_2OCH_3$; diglyme = $CH_3(OCH_2CH_2)_2OCH_3$). [c] This work (Table III). [d] 77 K data in ref 40. [e] 77 K data in ref 29 or 41. [f] 77 K data in ref 36.

The results will be discussed by class of compound and will be presented graphically.

In general, to construct the graphs in Figures 1–4, we have assumed that the highest NQR frequency of the specified equivalent chlorine atom observed in each compound corresponds to a chlorine atom which is not engaging in secondary bonding. The 77 K splittings used as the abscissa values for the plots are obtained by subtracting the other NQR frequencies observed from the highest frequency of the compound in question (eq 1). In many cases, of course, the splitting

$$\text{splitting of } n\text{th chlorine signal} = \nu_1 - \nu_n$$
$$n = 2, ..., j \text{ for } j \text{ frequencies} \qquad (1)$$

observed is simply due to nonbonding lattice effects: limits of 0.500 MHz splitting or of 2% of the NQR frequency (0.7–0.8 MHz) have been suggested for such lattice effects in covalent molecules.[25,28] Values in excess of these are common in mercurials.[5]

The value plotted along the ordinate represents the amount by which that splitting is reduced at 273 K or at room temperature (eq 2). We anticipate that in the presence of

$$\text{reduction of splitting} = (\nu_1 - \nu_n)_{T=77\,\mathrm{K}} - (\nu_1 - \nu_n)_{T=273\,\mathrm{K}}$$
$$n = 2, ..., j \text{ for } j \text{ frequencies} \qquad (2)$$

intermolecular secondary bonds in a class of compounds, there will be a statistical correlation of positive slope between ordinate and abscissa.

(*trans*-Chlorovinyl)mercuric Chloride (1). By its geometry, this compound can engage only in intermolecular interaction

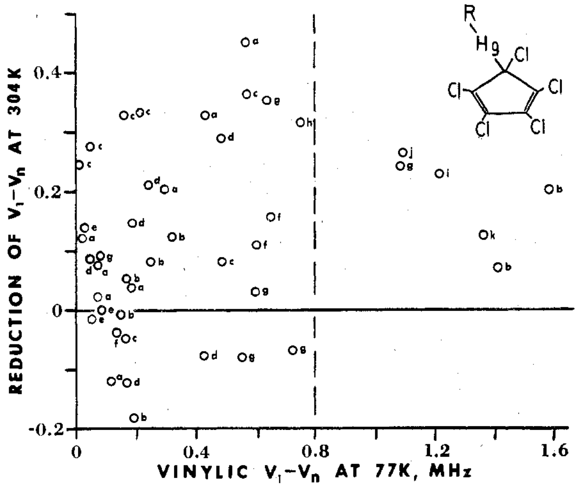


Figure 3. NQR frequency splittings at 77 K of vinylic chlorines of (pentachlorocyclopentadienyl)mercurials (**3**) compared with the reduction of those splittings at ambient temperature (about 304 K). Averaged vinylic NQR data used for compounds **3h**–**k**—see ref 5.

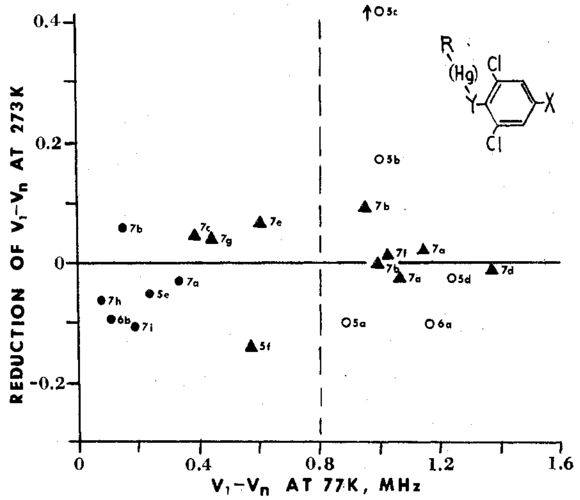


Figure 4. NQR frequency splittings at 77 K for 2,6-dichlorophenoxy (**5**, **7**) and 2,6-dichlorothiophenoxy (**6**) compounds compared with the reduction of those splittings at 273 K. Data for mercurials are shown with open circles, data for non-hydrogen-bonding chlorines in nonmercurials are shown with closed circles, and data for hydrogen-bonding chlorines in nonmercurials are shown with closed triangles.

Table III. Organochlorine NQR Data at Selected Temperatures

compd and 77 K lit. ref	assignt	^{35}Cl freq, MHz (*S*/*N* ratio in parentheses)		
		77 K	195 K	273 K
3g W1	Cl(5)	37.760 (5)	37.416 (3)	*a*
		37.591 (8)	37.273 (5)	37.00 (3)
	Cl(1234)	36.837 (8)	36.368 (5)	36.06 (4)
		36.524 (6)	36.093 sh	*a*
		36.457 (6)	36.107 (3)	*a*
		36.233 (9)	35.825 (5)	35.49 (3)
		36.120 (7)	35.645 (4)	35.28 (3)
		35.972 (6)	35.505 (4)	*a*
		35.881 (6)	35.609 (5)	*a*
		35.757 (10)	35.465 (5)	35.23 (3)
4a	Cl(345)	38.225 (6)	38.008 (2)	37.842 (2)
		38.225 (6)	37.973 (2)	37.777 (2)
		38.125 (3)	37.908 (2)	37.734 (2)
		38.078 (3)	37.860 (2)	37.669 (2)
		37.860 (3)	37.674 (2)	37.505 (2)
		37.720 (3)	37.562 (2)	37.428 (2)
	Cl(26)	36.641 (3)	36.418 (2)	36.230 (2)
		36.501 (2)	36.243 (2)	36.075 (2)
		36.435 (6)	36.167 (2)	35.997 (2)
		36.435 (6)	36.130 (2)	35.875 (2)
4a B2	Cl(345)	38.220 (6)		
		38.220 (6)		
		38.094 (3)		
	Cl(26)	37.828 (3)		
		36.421 (3)		
4a (Seyferth sample)	Cl(4)			37.76 (5)^b
	Cl(35)			37.59 (7)^b
	Cl(26)			35.93 (8)^b
4b B2	Cl(345)	38.297 (6)	38.073 (3)	37.880 (2)
		38.159 (6)	37.959 (3)	37.771 (2)
		38.057 (6)	37.846 (4)	37.656 (2)
	Cl(26)	36.968 (5)	36.756 (3)	36.573 (2)
		36.500 (5)	36.312 (3)	36.147 (2)
4c B2	Cl(345)	38.284 (3)	38.069 (1.5)	37.802 (1.5)
		38.193 (3)	37.925 (1.5)	37.69^c
		38.005 (4)	37.788 (2.5)	37.587 (2)
	Cl(26)	36.793 (4)	36.588 (2.5)	36.411 (2)
		36.330 (3)	36.166 (2)	36.04^c
4d	Cl(345)	38.152 (3)	37.936 (2)	37.754 (2)
		37.740 (3)	37.571 (2)	37.417 (2)
		37.362 (3)	37.168 (2)	37.015 (2)
	Cl(26)	36.717 (3)	36.514 (3)	36.343 (2)
		36.596 (3)	36.435 (3)	36.284 (2)
5a K4	Cl(6)	34.924 (2.5)	34.682 (2)	34.476 (2)
	Cl(2)	34.044 (2)	33.752 (2)	33.500 (2)
5b K4	Cl(6)	35.004 (4)	34.608 (2.5)	34.299 (2)
	Cl(2)	33.995 (6)	33.708 (4)	33.472 (2.5)
5c K4	Cl(6)	35.244 (3)	34.991 (3)^d	*d*
	Cl(2)	34.147 (7)	34.014 (6)^d	*d*
5d K4	Cl(6)	34.892 (4)	34.495 (3)	34.159 (1.5)
	Cl(2)	33.657 (7)	33.230 (5)	32.897 (2.5)

[a] These lines fade out gradually between 195 and 252 K, perhaps due to fluxional reorientation of the C_5Cl_5 ring (ref 44). Further work is planned to investigate this phenomenon. [b] Observed at room temperature on a Wilks spectrometer. Side bands present in the spectrum could have hidden additional small splitting. [c] Detected on a Wilks spectrometer at 0.6 °C. Accuracy ±0.06 MHz. [d] Frequencies listed were obtained at 110 K (isopentane slush bath); no spectrum was observed at higher temperatures.

of chlorocarbon chlorine and mercury. X-ray crystallography[45] indicates the presence of three types of molecule per unit cell, two of which have intermolecular Cl–Hg contacts. These two have frequencies at 77 K[46] which are split from the upper, noninteracting chlorine frequency by 1.060 and 1.722 MHz. These splittings are reduced (at 195 K) by 0.025 and 0.119 MHz, respectively, as we would expect for intermolecular secondary bonding.

(Trichloromethyl)mercurials (2). The results for nonmercurials of class **2**, shown with closed circles in Figure 1, show little change in splitting with a change in temperature. At first glance it is surprising that some of these compounds—**2h**, **2m**, **2n** and also the $\alpha,\alpha,\alpha,\omega$,-tetrachloroalkanes[47]—show splittings in excess of 0.8 MHz. Although the splitting in **2h** was originally attributed to intermolecular hydrogen bonding, all of these splittings have now been attributed to intramolecular electronic effects.[31,33,34,47]

The mercurials (shown with open circles in Figure 1) show larger splittings and a positive correlation of abscissa and ordinate. This suggests intermolecular secondary bonding. The crystal structure of **2c**[46] can variously be interpreted to indicate inter- or intramolecular interactions,[5] but the overall pattern of NQR frequencies is more rational if the interaction is assumed to be intermolecular.[5]

(Pentachlorocyclopentadienyl)mercurials (3). The temperature dependences of the allylic chlorines (chlorine number 5, Table I) cannot be rigorously analyzed by the methods used here, since chlorine 5 is unique, and neither intramolecular nor intermolecular interactions necessarily lead to NQR frequency splittings, even if there are two molecules per unit cell. We have previously noted[5] that compounds with lower allylic frequencies also tend to have less negative temperature dependences than those with high allylic frequencies. This hints at the presence of intermolecular secondary bonds, but the conclusion cannot be firm, because one cannot assume that in the absence of Cl–Hg interaction all allylic chlorines will have similar temperature dependences in all of the compounds studied.

Interpretations of splittings in the vinylic chlorines are complicated by the fact that the 1,4- and 2,3-vinylic chlorines are chemically inequivalent. In fact, a study of organic derivatives of **3** indicates that the two types of Cl are distinguishable by NQR only at very high and very low Taft σ^* values for R (i.e., in **3g**, for which σ^* is estimated to be −2.3).[48] Intramolecular secondary bonding could either augment or reduce the splitting of the 1,4 and 2,3 chlorines. But since the Hg atom is expected to be equidistant from the 1 and 4 chlorines, no further splitting can be generated by intramolecular secondary bonding. In fact the most common pattern is of four lines, one being well separated from the other three on the low-frequency side.[5] This pattern suggests intermolecular bonding.

Figure 2 presents the results of temperature-dependent NQR measurements for the vinylic chlorines of organic members of class **3**. There appears to be little systematic reduction of these splittings between liquid nitrogen and room temperature.

Figure 3 presents the data for the mercurials in class **3**. All splittings of greater than 0.5 MHz are reduced at room temperature, except two in **3g**, a compound in which much of the splitting should be due to chemical inequivalence. Hence temperature-dependence data for the mercurials of class **3**, although complicated by vinylic inequivalence, are consistent with patterns of intermolecular secondary bonding.

(2,6-Dichlorophenoxy)- and (Thiophenoxy)mercurials (5, 6). As in the previous classes, intermolecular interaction can again produce splittings of the frequencies of the 2 and 6 chlorines. In this class, provided a conformation about the C–O or C–S bond such as is drawn in Table I is adopted, intramolecular secondary bonding can also provide such a splitting. Hence the variable-temperature experiment can provide meaningful evidence to choose between inter- and intramolecular secondary bonding. Furthermore, such a conformation should be favored, both by intramolecular secondary bonding and by the increased conjugation of the oxygen or sulfur lone-pair electrons with the aromatic ring.

The NQR data for non-hydrogen-bonding ortho chlorines in nonmercurials of classes **5**, **6**, and **7** (solid circles in Figure 4) show the usual pattern of small splittings with no systematic reduction of these splittings at higher temperatures. Hydrogen bonding to the ring chlorine is a type of secondary bonding, and Kravtsov et al.[37] have studied the NQR spectra of several 4-substituted 2,6-dichlorophenols at various temperatures. Their results (triangles in Figure 4) show some large splittings, but the splittings are *not* regularly reduced at room temperature. This is consistent with the evidence[49] which indicates the presence of intramolecular hydrogen bonding to chlorine in this type of molecule.

The data for the mercurials (open circles in Figure 4) parallels that for hydrogen bonding: fairly large splittings not reduced at 273 K, suggesting intramolecular secondary bonding. This interaction has been proved to exist by X-ray crystallography in the case of phenylmercury 2-chloro-4-bromophenoxide,[50] but this compound was unsuitable for this NQR study since no splitting could result from the interaction. The NQR data for **5c** is anomalous: it could only be obtained at 77 and 111 K, due to rapid loss of signal intensity, and an unusually great temperature dependence of the frequencies was noted. Since many factors affect the temperature dependence of NQR frequencies, it is expected that anomalies such as this will occur, and it is not possible to assign its cause. It is worth noting, however, that the bulky ortho isopropyl groups in **5c** might hinder intramolecular secondary bonding and thus result in intermolecular bonding in this one compound.

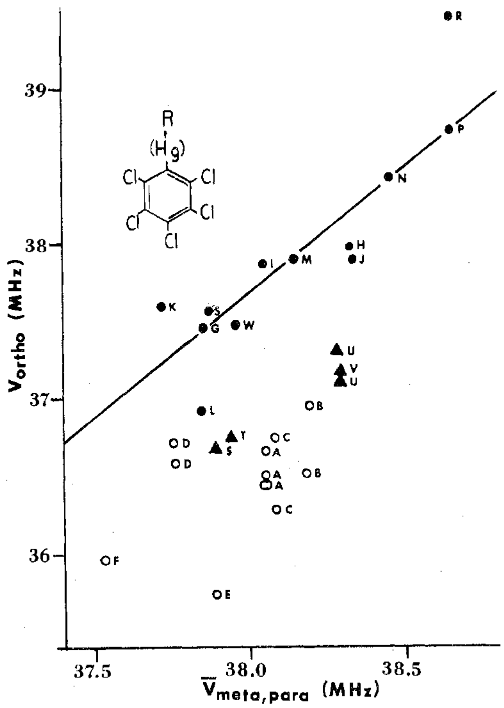


Figure 5. NQR frequencies of ortho chlorines of substituted pentachlorobenzenes (**4**) plotted against the average of the meta and para chlorine frequencies (at 77 K). Data for mercurials are shown with open circles, data for hydrogen-bonding chlorines in nonmercurials are shown with closed triangles, and *average* ortho chlorine frequencies for non-hydrogen-bonding nonmercurials are shown with closed circles. Letters refer to compounds listed in Table II, which includes literature references.

(Pentachlorophenyl)mercurials (4). In this series of mercurials the ortho chlorines fall sufficiently low in frequency to be readily distinguished from the meta and para chlorines. Any significant splitting of the ortho chlorines must correspond to intermolecular interactions, as intramolecular interactions will treat the two chlorines in the same manner, assuming that no additional ligands are bonded to the mercury in the C_6Cl_5 plane. But if both ortho chlorines engage in intermolecular interaction, no splitting need result. In fact, appreciable splitting is observed in only three cases: in the published spectrum of **4a**[40] and in **4b** and **4c**.[40] In the latter two cases the splitting is less than 0.8 MHz.

We were unable to reproduce the published spectrum of **4a**.[40] Using a large sample (10 g) of the commercial material, we obtained a weak ten-line spectrum at different temperatures. Recrystallization or sublimation did not alter this. On the other hand, a sample provided to us gave a different (three-line) spectrum. Hence it appears that different phases may exist. However neither spectrum we obtained showed the substantial (1.3 MHz) splitting of the ortho-chlorine frequencies reported in the literature.

The splitting of the ortho chlorines in **4b** and **4c** was investigated by variable-temperature NQR. The splittings of the two frequencies in **4b** and **4c** were reduced at higher temperatures by small amounts (0.06 and 0.19 MHz, respectively).

Since intramolecular interactions cannot produce a splitting in these compounds and intermolecular interactions need not, we have adopted a different analysis of the data of the ortho chlorines. The average frequencies of the ortho chlorines are plotted against the average frequencies of the meta and para

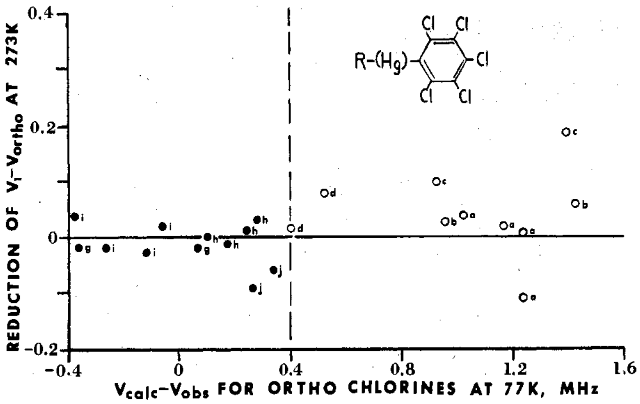


Figure 6. Frequency shifts of ortho chlorines of substituted pentachlorobenzenes (**4**) at 77 K, as determined by eq 4, compared to the reduction of the splitting of the ortho and the highest meta or para chlorine which results on going from 77 to 273 K. Data for mercurials are shown with open circles, and data for nonmercurials are shown with closed circles.

chlorines for a number of organic pentachlorobenzenes (solid circles in Figure 5). The correlation expressed in eq 3 is

$$\bar{\nu}_{\text{ortho}} = [1.602\bar{\nu}_{\text{meta,para}} - 23.16 \pm 0.36]\ \text{MHz} \qquad r = 0.827 \tag{3}$$

obtained. In comparison to the values expected from (3), both the potentially hydrogen-bonded species (solid triangles) **4s–v** and the mercurials (open circles) **4a–f** show lower ortho-chlorine frequencies than would be predicted by eq 3.

The ortho-chlorine data for the mercurials and some model organic pentachlorobenzenes are then plotted in Figure 6, as a shift from the expected average ortho-chlorine frequency:

$$\text{shift at 77 K} = \bar{\nu}_{\text{ortho}}(\text{calcd from eq 3}) - \nu_{\text{ortho}}(\text{obsd}) \tag{4}$$

The reduction in splitting is measured not from the highest ortho chlorine, which is probably also engaged in the interaction, but from the highest of the meta- or para-chlorine frequencies. This assumes similar amplitudes of oscillation of all chlorines in the ring, which is not necessarily true, but it appears to be justified from the data on the model compounds **4g–i**. Indeed, in the existing temperature-dependence data, all chlorines in each derivative of **4** show remarkably similar, and small, temperature dependences.

In Figure 6 the data for the mercurials show little deviation from the line of zero reduction of splitting, suggesting that the interaction is intramolecular. Although the interaction appears to be quite significant in magnitude, one must remember the approximations involved in treating the data for **4** and the relatively large error in eq 3. There may also be a contribution from the fact that the van der Waals radius of mercury is apparently[5] smaller than those of the second-row elements in the R groups of **4g–i**.[51] Some of the frequency lowering might then be due to relief of the steric strain which may exist in hexachlorobenzene and its derivatives.[25,52]

Pressure Dependence of NQR Spectra. In work on the group 5 metal trihalides, Gillies and Brown[16–18] and Ainbinder et al.[19–21] have demonstrated that anomalous pressure dependence results from intermolecular Sb–Cl and Bi–Cl interaction. The NQR frequency ν varies from its 0 K and zero-hydrostatic-pressure value as a result of increasing amplitudes of oscillation θ of the quadrupolar atoms and of volume dependence of ν_0

$$\nu = \nu_0(1 - \tfrac{3}{2}\langle\theta^2\rangle) \tag{5}$$

The change in ν with pressure may be written

$$\frac{\partial\nu}{\partial P} = \frac{\partial\nu_0}{\partial P}\left(1 - \frac{3}{2}\langle\theta^2\rangle\right) - \frac{3}{2}\nu_0\frac{\partial\langle\theta^2\rangle}{\partial P} \tag{6}$$

Table IV. Pressure Dependences of ^{35}Cl NQR Frequencies

	data at 250.5 K		data at room temp		
compd	freq, MHz	$\partial\nu/\partial P^a$	freq, MHz	$\partial\nu/\partial P^a$	T, K
2a	37.938	+0.88	37.668	+1.12	296.7
	37.068	+0.50	36.838	+0.80	293.6
	36.446	+0.42	36.221	+0.73	294.1
4b	37.938	+0.09	37.828	+0.14	293.6
	37.827	0.00	37.716	+0.08	295.1
	37.713	+0.07	37.608	+0.11	294.6
	36.622	+0.12	36.509	+0.20	294.6
	36.197	−0.03	36.087	+0.1	296.1

[a] In units of kHz/MPa.

$\partial\langle\theta^2\rangle/\partial P$ is inherently negative since increasing pressure must decrease thermal oscillation amplitudes, and hence the second term is inherently positive. In an "ideal" molecular crystal where intermolecular interactions are very weak or nonexistent, $\partial\nu_0/\partial P$ should be very small or zero, since changing intermolecular distances due to compression should not affect the electric field gradient within a molecule. Hence the pressure dependence $\partial\nu/\partial P$ of a truly molecular compound should be positive. If intermolecular secondary bonding occurs, compressing the compound will affect the value of ν_0. The value of $\partial\nu_0/\partial P$ has been postulated to be negative,[18] and this effect may be large enough to override the positive second term. This occurs in the more strongly interacting chlorine Cl(2) of $BiCl_3$.[16–22]

Pressure-dependent measurements were carried out at two temperatures each for compounds **2a** and **4b**; results are presented in Table IV. The two lower frequencies in **2a**, in which the splitting and temperature dependence suggest intermolecular interaction, show significantly lower positive pressure dependences, as expected. In the case of **4b**, which showed a marginally significant splitting of the ortho-chlorine frequencies and a marginally significant reduction of this splitting at 273 K, the pressure dependences of all five chlorine resonances are approximately the same and provide no conclusive evidence concerning intermolecular secondary bonding.

The comparison of the pressure coefficients in **4b** and **2a** is of interest. Temperature-dependence data suggest that there is intermolecular secondary bonding in **2a** but not in **4b**, but $(\partial\nu/\partial P)_T$ is considerably more positive for **2a**. However, $(\partial\nu/\partial P)_T$ is a strong function of temperature in **2a**, and extrapolation to low temperatures indicates that $(\partial\nu/\partial P)_T$ for **2a** should become negative at very low temperatures. The reason for the strong temperature dependence of $(\partial\nu/\partial P)_T$ in **2a** remains obscure, and more work at low temperatures is required.

Conclusions

On theoretical grounds it may be argued that there should be low NQR frequencies for organochlorines which engage in weak secondary bonding with metal atoms. A statistical test is suggested for learning whether the bonding is intermolecular or intramolecular in a class of compounds: NQR splitting caused by intramolecular secondary bonding is expected to be independent of temperature and pressure; splitting due to intermolecular bonding is expected to be increased at lower temperatures and higher pressures.

These ideas have been applied in a series of mercury derivatives of chlorocarbons in which intramolecular interaction, if present, would result in three-, nonplanar four-, planar four-, and five-membered rings (classes **2** and **3**, **3**, **4**, and **5**, and **6**, respectively). The results support the notion that the interactions present are intermolecular in classes **1**, **2**, and **3**, and intramolecular in classes **4**, **5**, and **6**.

These results do not necessarily rule out some of the mechanisms suggested for the reactions mentioned in the Introduction, since NQR measures ground-state phenomena whereas the proposed mechanisms involve small-ring formation in a higher energy transition state. But these results might bear on questions of geometry of the transition state.

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Registry No. **2a**, 67951-82-0; **3g**, 67951-83-1; **4a**, 1043-49-8; **4b**, 941-77-5; **4c**, 30615-32-8; **4d**, 67951-73-9; **5a**, 21524-46-9; **5b**, 21571-80-2; **5c**, 21524-47-0; **5d**, 21524-51-6.

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Bis(diphenylphosphino)ethane Complexes of Iron

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The chemistry of a variety of bis(diphenylphosphino)ethane (DPPE) complexes of iron has been investigated. Zerovalent, five-coordinate complexes of iron have been prepared with CO and phosphorus ligands. Reactions with acetylenes give a series of hydrido acetylide complexes. Reaction with cyclopentadiene results in the loss of one DPPE to give Fe(DPPE)(Cp)H. Reactions with other compounds having activated C–H bonds give Fe(DPPE)$_2$H$_2$. Reactions with tetracyanoethylene and tetracyanoquinodimethan involve electron transfer. Steric effects are shown to be important in determining the stability and geometry of the complexes.

Introduction

In a series of papers,[1–4] we have described the chemistry of Fe(DMPE)$_2$H(C$_{10}$H$_7$)[5] (**1**). The studies included reactions with Lewis base ligands, L, such as phosphorus ligands, olefins, disubstituted acetylenes, and diazenes to give five-coordinate, zerovalent complexes, Fe(DMPE)$_2$L, and the reaction with hydrogen to give Fe(DMPE)$_2$H$_2$[2] (**2**). The cleavage reactions of C–H bonds involving hydrogen cyanide, monosubstituted